CCSF PHYC 4D Lecture Notes

Karl M. Westerberg

Chapter 9
Molecular Structure

Introduction

- A molecule is a small group of atoms bound together by some bonding mechanism. A full quantum mechanical treatment of the molecule would consist of solving the Schrodinger Equation for the full wave function, which would be a function of the positions of all N_e electrons and N_a nuclei belonging to the molecule. This would require writing down the full potential energy function and solving a very difficult partial differential equation for the $N_e + N_a$ particle wave function. All of chemistry would follow from such a treatment.

- An even more complete calculation would treat the protons and neutrons separately (or to be even more complete, the quarks making up those particles would be treated separately), along with the strong interaction which binds those particles together to form nuclei. This treatment would include all nuclear effects, as well as all chemical effects.

- Neither of these treatments is particularly tractable. Even the former model with each nuclei treated as a single particle would be difficult to solve. Fortunately, we do not need such a sophisticated treatment to understand the basics of molecular bonding.

- We will instead adopt a "semi-classical" approach, where the N_a nuclei are, at least initially, treated classically as point particles located at fixed points in space $(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_{N_a})$, acting as sources of electric fields which interact with the electrons.

- The N_e electrons would then be treated quantum mechanically. The electronic state is defined by the electronic wave function $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N_e})$. The stationary states would be determined by solving the Schrodinger Equation using a potential energy function that includes electron-nucleus and electron-electron interactions.

- The electronic ground state and its energy would naturally depend on the locations of the nuclei, and so would be a function of the nuclei positions. If we add the electronic ground state energy to the electrostatic potential energy associated with nucleus-nucleus interactions, we obtain an effective potential energy function for the molecule, which can be expressed as a function of the nuclei positions: $U_{\text{eff}}(\vec{R}_1, \ldots, \vec{R}_{N_a})$.

- At this point, we may choose to treat the motions of the nuclei classically using this potential energy function. The configuration $(\vec{R}_1, \ldots, \vec{R}_{N_a})$ which minimizes this effective potential energy function would then be the expected equilibrium configuration for the molecule.

- Treating the nuclei classically is a crude approximation, but is not a terrible one, since the nuclei have a much larger mass than the electron. Confining a nucleus to a small "box" requires much less energy than confining an electron to that same box, and so ignoring the uncertainty principle for the nuclei would not be absurdly wrong.

- Nevertheless, we could treat the nuclei quantum-mechanically by using the effective potential energy function to write down a Schrodinger Equation for the *nuclear* wave function $\Psi(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_{N_a})$.

- This is still an approximation to the full quantum-mechanical treatment of the molecule, since the electronic state is assumed to always occupy its ground state based on whatever positions the nuclei happen to occupy at any given moment. This is not an unreasonable assumption, again in light of the fact that nuclear masses are much greater than the electron mass.

- Many computer codes which perform quantum chemistry calculations have used this semi-classical approach with great success.

- In the first part of this chapter, we discuss various types of chemical bonds, treating the nuclei as located at fixed positions and focussing on the electronic states.

- In the second part of this chapter, we then discuss vibrational, rotational, and translational modes of these molecules, essentially treating the nuclei quantum mechanically.

The single-electron molecule

- Perhaps the simplest molecule to consider is the singly-ionized hydrogen molecule H_2^+. This molecule (technically an ion, since it has a net charge) consists of two protons and one electron. In accordinance with the semi-classical approach, we assume that these protons are located at fixed

points in space a distance R apart. Let's begin with the protons very far apart: $R \gg a_0$.

- The electron should now be treated quantum mechanically. Its wave function is given by $\psi(\vec{r})$. Of course this electron could be anywhere — it could be flying around in some remote area far away from either proton. However, our goal is to determine the ground state energy of this electron, the configuration where it has the lowest total energy. Clearly, that occurs when the electron is bound to one of the protons in its hydrogen atom ground state.

- Evidently, there are two ground states for the electron, ψ_1 and ψ_2, where the electron is bound to proton 1 and 2, respectively. Actually, there are four ground states if we include electron spin — but let's not, at least for now. The two wave functions are sketched in Fig. 9.1 (p. 259) of the textbook. The energy of each of these electronic configurations is given by $-E_0$, where $E_0 = 13.6\,\text{eV}$.

- As the protons are moved closer (but not too close, yet), an interesting thing happens. The potential energy function for the electron is depicted in Ch9:p1, and is in the form of a double well with a finite barrier between the two wells. The states ψ_1 and ψ_2 are no longer stationary states, because an electron bound to one proton can *tunnel* through the barrier over to the other proton. If $\psi = \psi_1$ at $t = 0$ (implying that the electron starts out bound to proton 1), then ψ will in general be some mixture of ψ_1 and ψ_2 at later times due to this tunnelling.

- The essential features of the double well potential can be worked out by treating the electronic state as a two-state system, where at any given time, the state of the electron is given by

$$\psi(\vec{r}, t) = c_1(t)\psi_1(\vec{r}) + c_2(t)\psi_2(\vec{r})$$

The result of this analysis (given in an appendix) is that there are two stationary states given by ψ_+ and ψ_-, where

$$\psi_\pm(\vec{r}) = \beta_\pm(\psi_1(\vec{r}) \pm \psi_2(\vec{r}))$$

The energy levels for these two states are given by $E_\pm$ and are separated from one another by an amount that depends on the tunnelling rate. As

the protons are brought closer, the difference between the two energy levels ($|E_+ - E_-|$) increases. The coefficients $\beta_\pm$ are determined by normalization and will equal $1/\sqrt{2}$ when the two protons are far apart.

- The two wavefunctions ψ_+ and ψ_- are plotted in Fig. 9.2 (p. 259) of the textbook, along with their corresponding probability densities in Fig. 9.3. In each case, the electron is *shared* between the two protons; the electron is as likely to be found near proton 1 as it is to be found near proton 2.

- Exactly how this electron is shared depends on which state, ψ_+ or ψ_-, we have. Since the original states ψ_1 and ψ_2 are spherically symmetric, and by convention, positive everywhere, it follows that for ψ_+ the electron probability amplitude interferes *constructively* in the region between the protons. In the state ψ_+, the electron is very likely to be found in between the protons. On the other hand, for ψ_- the electron probability amplitude interferes *destructively* in the region between the protons, and so the electron is unlikely to be found there. In the state ψ_-, the electron tends to hang out on one side or the other of the protons, but not between them.

- Which state is lower energy? This can be determined by noting that when the electron is between the protons, it is relatively close to both of them, and thus the electron-proton contribution to the electrostatic potential energy is a relatively large negative contribution. On the other hand, when the electron is to one side or the other of the protons, it is reasonably close to one proton, but much farther away from the other, so the negative contribution to the electrostatic potential energy is not as great. It makes sense that $E_+ < E_-$, and that ψ_+ has a lower energy than ψ_-.

- If we bring the protons really close, then the potential energy wells merge (Ch9:p1), and it no longer makes sense to regard them as separate wells. It is still the case, however, that there are two stationary states, one that we can call ψ_+, for which the electron spends considerable time between the protons, and the other that we can call ψ_-, for which the electron spends relatively little time between the protons. The energy levels for the electronic states continue to diverge, with ψ_+ lower energy than ψ_-.

The states ψ_1 and ψ_2 that we would use to generate $\psi_\pm$ would no longer be hydrogen atom ground states surrounding one of the protons, but would now be distorted due to the close proximity of the other proton.

- Various energy contributions are plotted as functions of R in Fig. 9.4 (p. 260) of the textbook. The energies E_+ and E_- represent the energy of the electronic configurations ψ_+ and ψ_-, respectively, and were presumably obtained from a numerical solution to the Schrodinger Equation. The electrostatic potential energy of the proton-proton repulsion is given by U_p, and the combined effective potential energy for $\psi_\pm$, given by

$$U_{\text{eff},\pm} = E_\pm + U_p$$

  is also plotted as a function of R.

- Bonding is determined by the effective potential energies of the two states $U_{\text{eff},+}$ and $U_{\text{eff},-}$. Both $U_{\text{eff},+}$ and $U_{\text{eff},-}$ approach $-E_0$ as $R \to \infty$. $U_{\text{eff},-}$ increases as R decreases, and thus depicts a situation where there is always a net repulsion between the two protons. Evidently no bound state can result for H_2^+ using the ψ_- electronic configuration. However, $U_{\text{eff},+}$ first decreases as the protons are brought closer together, until an equilibrium point is reached at around $R = 2a_0$. This represents the ground state of the H_2^+ ion. The effective potential energy at this value of R is $2.7\,\text{eV}$ below the effective potential energy at $R \to \infty$, and thus represents the binding energy of the hydrogen ion. I am assuming that this is in excellent agreement with experiment.

- It is interesting that $U_{\text{eff},+}$ bottoms out at around $R = 2a_0$, which is twice the radius of the hydrogen atom. It kind of makes sense that there would be a diminishing return in terms of E_+ decreasing as R decreases. Once $R = 2a_0$ is crossed, the constructive interference of ψ_1 and ψ_2 in the region between the protons sort of maxes out, as the center point coincides with the point of maximum radial probability density for both hydrogen atom wave functions. Mind you, E_+ continues to decrease as R falls below this value, but that is more than compensated for by the fact that U_p increases without bound as $R \to 0$. By contrast, E_+ approaches a finite limit (the helium ion ground state energy) as $R \to 0$. It is inevitable that $U_{\text{eff},+} = E_+ + U_p$ will eventually increase without

bound as R is decreased to zero.

- A technical point about the two-state model for the double well potential. If we define the energy of each of the infinitely separated single wells to be E_0, then the energies of the two stationary states of the finitely separated wells are given by $E_0 \pm \epsilon$, where ϵ can be related to the size of the barrier between them (as the barrier comes down, ϵ increases). This suggests that one state increases in energy and the other state decreases in energy as the barrier is reduced, and that the two energies differ from E_0 by the same amount.

- If one looks at E_+ and E_- as a function of R for the hydrogen ion, one can see that this does *not* occur; both E_+ and E_- decrease as R is initially decreased from ∞. This is for the simple reason that an electron bound to one proton is still attracted to the other proton, and that gives rise to a negative contribution to the energy of the state which increases as R decreases. This effect is not captured in the generic two-state model for the double-well potential. However, if one adds the proton-proton contribution to the electrostatic potential energy, that will offset the electron-"other proton" interaction. Thus, one finds that the *effective potential energy functions* $U_{\text{eff},\pm}$ indeed follow the general trend for double well potentials: $U_{\text{eff},-}$ is as much higher than $-E_0$ (the value at $R \to \infty$) as $U_{\text{eff},+}$ is below $-E_0$, at least for large enough R. Of course, this relationship breaks down as R approaches zero, because the wells merge and it no longer makes sense to treat the hydrogen ion as a double well potential.

Many electron molecules

- When discussing many-electron atoms in Chapter 8, we noticed that, in spite of the strong interactions among the various electrons, it was possible to think of each electron as separately belonging to a single-electron state, in the sense that the stationary states for the N_e-electron system can be approximated as product states of single-electron wave functions (to be more precise: anti-symmetric combinations of product states, as the electrons are identical fermions). The single-electron states were described using the same quantum numbers that were appropriate for the

single-electron atom, but the states themselves and the energies of those states were different because of the interactions among the electrons.

- The Pauli Exclusion Principle prevents more than one electron from occupying a given single-electron state at any given moment, and so, generally speaking, the ground state of the atom is determined by placing electrons in an atom so as to fill up the lowest energy single-electron states.

- It should not be a surprise that the same thing happens with molecules. Really, the only difference between a molecule and an atom is the presense of more than one nucleus in a molecule.

- Consider once again the H_2^+ ion discussed in the previous section. We found that we could combine the two $1s$ subshells of the hydrogen atom to produce four possible electronic states for H_2^+, two states (one for each spin state) associated with ψ_+, the lower energy "bonding" states, and two states associated with ψ_-, the higher energy "anti-bonding" states. Of course there are other states that can be formed by combining the two $2s$ subshells, or the two $2p$ subshells, and so on, but those states would be of considerably higher energy.

- The ground state electronic configuration naturally would be to have the one single electron occupying one of the bonding states associated with ψ_+. Since the effective potential energy is minimized at $R = 2a_0$, and is less than the effective potential energy at $R \to \infty$, the hydrogen ion is stable in this configuration; the two hydrogens are bonded together and the single electron occupying one of the bonding states is shared between the two atoms.

- Consider what happens now if we add an additional electron to the system, creating the neutral H_2 molecule. In this case, we can think of the two electrons each occupying one of the four states discussed above. Yes, the states themselves and their energies will have to be adjusted because of the presence of the second electron, but we should still expect two lower energy "bonding" states and two higher energy "anti-bonding" states available for the electrons. Since there are two bonding states available (thanks to there being two spin states), it should be expected

that the electronic ground state of H_2 involves having both electrons occupy the bonding state.

- If having one electron shared between two atoms in a bonding state reduces the effective potential energy (compared to having the two atoms far apart), then having *two* electrons in a bonding state should, in effect, pay double. Indeed, that appears to be the case. The effective potential energy for the H_2 molecule is plotted in Fig. 9.6 (p. 261) of the textbook. The binding energy associated with the "bonding" case (where both electrons occupy the bonding states) is 4.5 eV, which is higher than, but not quite double the binding energy of the hydrogen ion. The two electrons occupy the same spatial state, and therefore repel quite strongly; this might explain why the binding energy is not quite doubled.

- One should also notice that the equilibrium distance between the protons (where U_{eff} is minimized) with H_2 is somewhat less than with H_2^+. With two electrons now spending a lot of time between the protons, the bond should be stronger, so it makes sense that the atoms will be bound tighter together. One can also reason numerically: when R is reduced, the benefit of reducing E_+ is doubled in H_2 as compared to H_2^+, but the penalty for increasing the electrostatic potential energy associated with proton-proton repulsion is unaffected by the presense of the second electron.

- I can only presume that the "anti-bonding" graph plotted in Fig. 9.6 is for the case where the two electrons occupy the anti-bonding states. Of course no bonding is expected in that case, since there is an energy *penalty* associated with bringing the protons in from ∞ when the two electrons occupy the anti-bonding states.

- The hybrid case, where one electron is in a bonding state and the other electron is in the anti-bonding state, would appear to be a wash; energy benefits associated with the bonding state should be nearly canceled exactly by energy penalty associated with the anti-bonding state, resulting in a relatively flat U_{eff} curve. This should indeed be the case, at least for $R \gg a_0$, in light of the two-state model for the double well potential. However, as R is reduced to on the order of $2a_0$, one should expect a net penalty, since the two electrons repel each other and other effects related

to the breakdown of the two-state double well model. I would expect the graph of U_{eff} in this case to resemble a relatively flat line coming from ∞, and then slowly increasing once $2a_0$ is approached. There would be no stable equilibrium for the H_2 molecule associated with this electronic configuration.

- Molecules with three or four electrons can also be analyzed. In a three-electron molecule, the electronic ground state should include two electrons occupying the bonding states and one electron occupying an anti-bonding state. This is expected to result in a stable molecule, with binding energies similar to the H_2^+. This indeed happens with the di-helium ion (He_2^+). Four-electron molecules are not expected to be stable, since two electrons would go into the bonding state and two electrons would go into the anti-bonding state. Again, a slight net penalty is expected, resulting in no stable equilibrium configuration. Thus He_2 is not a stable molecule.

ss covalent bonding

- something. . .

p orbitals

- something. . .

sp and pp covalent bonding

- something. . .

sp hybrid states

- something. . .

Covalent bonds involving higher l states

- something...

Ionic bonds

- something...

Molecular vibrations

- something...

Molecular rotations

- something...

Molecular translations

- something...

Molecular spectrum

- something...

Appendix: Double well potentials (2-state)

- A double well potential is a potential energy function which confines the particle to one of two regions with a rather significant potential energy barrier in between. From the point of view of classical physics, the particle will be trapped in one well or the other, with no possibility of crossing the barrier to get from one well to the other. In quantum mechanics, the particle can tunnel through the barrier and pass back and forth between the two wells.

- An example of a double well potential is the potential energy function for an electron that is attracted to two fixed protons, as in the H_2^+ ion (see Ch9:p1). Assuming that the protons are far enough apart, the electron will essentially be confined to one of two wells (one well surrounding each proton), with a significant barrier between them. Although this barrier all but disappears when the protons reach their equilibrium distance apart, there is still much insight to be gained by studying double well potentials in order to understand how the possibility of tunnelling affects the wave functions and energy levels associated with the stationary states of the electron.

- The essential features of the double well potential can be worked out by treating it as a two-state system. Suppose ψ_1 and ψ_2 represent the ground states of the corresponding single well potential around wells 1 and 2, respectively. We will assume that the two wells are symmetrical, so that the ground state energy associated with the two wells are the same value. Let that value be E_0.

- The approximation that we are making is that, at any given time, the system should be in a state that is in general a linear combination of ψ_1 and ψ_2. Thus, the general state is given by

$$\psi = c_1 \psi_1 + c_2 \psi_2$$

That state is determined by the coefficients c_1 and c_2, and can be written as a two-dimensional column vector

$$\psi = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Operators that operate on this state could then be expressed as 2×2 *matrices*. Note that the column vectors corresponding to ψ_1 and ψ_2 are $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$, respectively.

- We expect this approximation to be a good one whenever the barrier is significant, since in such cases, the presense or absense of one well will have little impact if the particle is presently confined to the other well.

- In fact, let's begin by assuming that there is *no* barrier penetration — the barrier is impenetrable (i.e., either it is very long or very high). In this case, we expect ψ_1 and ψ_2 to be stationary states satisfying

$$\hat{H}\psi_1 = E_0 \psi_1 \qquad \hat{H}\psi_2 = E_0 \psi_2$$

which can be written in terms of column vectors

$$\hat{H}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = E_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \hat{H}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = E_0 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Evidently, the Hamiltonian matrix is given by

$$\hat{H} = \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix}$$

- Now suppose that the barrier is penetrable. To understand what effect this has on the Hamiltonian, recall what the time-dependent Schrodinger Equation says:

$$\frac{d\psi}{dt} = -\frac{i}{\hbar}\hat{H}\psi$$

Suppose the particle is confined to well 1 at $t = 0$. This implies that $\psi(0) = \psi_1$. Because of tunnelling, we should expect that $\psi(t)$ for $t > 0$ to be some mixture of ψ_1 and ψ_2. This requires that $\hat{H}\psi_1$ must involve some mixture of ψ_1 and ψ_2, and so the off-diagonal elements of the Hamiltonian matrix will no longer be zero.

- In fact, the two off-diagonal elements *must* be complex conjugates of one another — there is a requirement on all operators (including the Hamiltonian) which represent observable quantities that they be *Hermetian*

conjugate. In other words, $\hat{H}_{ji} = \hat{H}_{ij}^*$. Thus, the Hamiltonian must be of the form

$$\hat{H} = \begin{pmatrix} E_0 & \epsilon e^{i\phi} \\ \epsilon e^{-i\phi} & E_0 \end{pmatrix}$$

- The constant ϵ is a positive real number, and is a measure of the penetrability of the barrier. The more impenetrable the barrier, the smaller ϵ is. Of course $\epsilon = 0$ when the barrier cannot be penetrated at all. The constant $e^{i\phi}$ is a phase factor which we will discuss later.

- Now that we have the Hamiltonian, we should be able to find the stationary states, and their corresponding energies. Evidently, ψ_1 and ψ_2 are not stationary states themselves, because of barrier penetration. To find the stationary states, we need to solve the time-independent Schrodinger Equation, $\hat{H}\psi = E\psi$, which can be written in terms of matrices as an *eigenvector/eigenvalue* problem:

$$\begin{pmatrix} E_0 & \epsilon e^{i\phi} \\ \epsilon e^{-i\phi} & E_0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

This can be rewritten

$$\begin{pmatrix} E_0 - E & \epsilon e^{i\phi} \\ \epsilon e^{-i\phi} & E_0 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

- Of course, $c_1 = c_2 = 0$ is always a solution to the above equation, no matter what E is, but $\psi = 0$ is not a properly normalized state. In order to find a solution for $\psi \neq 0$, the matrix on the left side must be *singular*, and thus its determinant must be zero. This will allow us to solve for the allowed energies E:

$$\begin{aligned} 0 &= \det \begin{pmatrix} E_0 - E & \epsilon e^{i\phi} \\ \epsilon e^{-i\phi} & E_0 - E \end{pmatrix} \\ &= (E_0 - E)^2 - (\epsilon e^{i\phi})(\epsilon e^{-i\phi}) \\ &= (E_0 - E)^2 - \epsilon^2 \end{aligned}$$

It follows that $(E - E_0)^2 = (E_0 - E)^2 = \epsilon^2$, and so the two allowed values of energy are given by

$$E = E_0 \pm \epsilon$$

- To find the stationary state corresponding to each value of energy, we plug E back into the matrix equation above and solve for c_1 and c_2. Since the matrix will be singular, there will be an entire one-dimensional family of solutions (not just $c_1 = c_2 = 0$). We will choose one of them by imposing a normalization condition.

- Carrying this out, we get

$$
\begin{aligned}
0 &= \begin{pmatrix} E_0 - (E_0 \pm \epsilon) & \epsilon e^{i\phi} \\ \epsilon e^{-i\phi} & E_0 - (E_0 \pm \epsilon) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \\
&= \begin{pmatrix} \mp\epsilon & \epsilon e^{i\phi} \\ \epsilon e^{-i\phi} & \mp\epsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \\
&= \epsilon \begin{pmatrix} \mp 1 & e^{i\phi} \\ e^{-i\phi} & \mp 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}
\end{aligned}
$$

Dividing out ϵ and performing the matrix multiplication yields two equations:

$$
\mp c_1 + e^{i\phi} c_2 = 0 \qquad e^{-i\phi} c_1 \mp c_2 = 0
$$

As expect, these equations are redundant, and are both equivalent to

$$
c_2 = \pm e^{-i\phi} c_1
$$

- If we assume that ψ_1 and ψ_2 are properly normalized states, we can interpret c_1 and c_2 in terms of the probability of finding the particle in well 1 or well 2 at any given time. In this case, the probability of finding the particle in well 1 is $|c_1|^2$ and the probability of finding the particle in well 2 is $|c_2|^2$. These probabilities must add to 1, leading to the normalization condition

$$
1 = |c_1|^2 + |c_2|^2 = |c_1|^2 + |\pm e^{-i\phi} c_1|^2 = |c_1|^2 + |c_1|^2 = 2|c_1|^2
$$

It follows that $|c_1| = 1/\sqrt{2}$, and so (up to an arbitrary overall phase), the stationary states are given by

$$
\psi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm e^{-i\phi} \end{pmatrix} = \frac{1}{\sqrt{2}} (\psi_1 \pm e^{-i\phi} \psi_2)
$$

- Throughout this analysis, the upper sign corresponded to the higher energy and the lower sign corresponded to the lower energy. Thus, to

spell things out clearly, we have two stationary states, the low-energy state

$$\psi_{\text{low}} = \frac{1}{\sqrt{2}}(\psi_1 - e^{-i\phi}\psi_2) \qquad E_{\text{low}} = E_0 - \epsilon$$

and the high-energy state

$$\psi_{\text{high}} = \frac{1}{\sqrt{2}}(\psi_1 + e^{-i\phi}\psi_2) \qquad E_{\text{high}} = E_0 + \epsilon$$

- If we compare this result to what we know about the solution to the hydrogen ion H_2^+, we find that it is appropriate to choose the phase $e^{i\phi} = -1$. Evidently, this phase depends on the particulars of the double well potential, as well as the relative phase between ψ_1 and ψ_2. If we are willing to redefine ψ_2 (or ψ_1) by a phase factor (this does not affect its normalization or its status as the ground state of the corresponding single well potential), then we could have eliminated the phase $e^{i\phi}$ altogether. However, we used the hydrogen atom ground state solutions for ψ_1 and ψ_2, and chose their phases to make them both positive real functions. This imposes a phase relationship between ψ_1 and ψ_2, and thus the phase factor $e^{i\phi}$ must be included.

- There are two things to note here:

  - The energy levels, which were both E_0 when the barrier was impenetrable, split into two levels, one of them *higher* than E_0 and the other one *lower* than E_0. In fact, both levels shift by the same amount, ϵ. This energy level splitting is entirely due to barrier penetration, and increases as the barrier becomes more penetrable (ϵ increases as the barrier comes down).

  - The stationary states themselves both involve the particle spending equal amounts of time in each well. This is to be expected, since the wells were assumed to be equivalent.

- To gain further insight into the barrier penetration, and to assign a physical meaning to the value of ϵ, let's now consider the time-dependent case. Let us suppose that the particle is known to be confined in well 1 at $t = 0$. That is,

$$\psi(0) = \psi_1$$

What is the state $\psi(t)$ at some later time $t > 0$? We cannot expect that state to be $\psi_1 e^{-i\omega t}$, since ψ_1 is not a stationary state. In fact, because of tunnelling, it would be unreasonable to expect the particle to remain in well 1 indefinitely.

- The correct solution involves first writing the initial state as a linear combination of the two stationary states. In fact, if we add ψ_{low} and ψ_{high}, the ψ_2's cancel out, leaving something proportional to ψ_1. It is a simple matter to show that

$$\psi(0) = \psi_1 = \frac{1}{\sqrt{2}}(\psi_{\text{low}} + \psi_{\text{high}})$$

- Now, if the initial state of the system had been a stationary state ψ_E, with energy E, then the full time-dependence would have been $\psi(t) = \psi_E e^{-i\omega t}$, where $\omega = E/\hbar$. Since the time-*dependent* Schrodinger Equation is linear, it follows that the full time dependence of our given initial state is

$$\psi(t) = \frac{1}{\sqrt{2}}(\psi_{\text{low}} e^{-i(E_{\text{low}}/\hbar)t} + \psi_{\text{high}} e^{-i(E_{\text{high}}/\hbar)t})$$

- Plugging in for ψ_{low} and ψ_{high} in terms of ψ_1 and ψ_2 again, and plugging in values for E_{low} and E_{high}, yields (after a bit of effort)

$$\begin{aligned}
\psi(t) &= e^{-i(E_0/\hbar)t}\left(\psi_1 \cos((\epsilon/\hbar)t) - ie^{-i\phi}\psi_2 \sin((\epsilon/\hbar)t)\right) \\
&= e^{-i(E_0/\hbar)t}\begin{pmatrix} \cos((\epsilon/\hbar)t) \\ -ie^{-i\phi}\sin((\epsilon/\hbar)t) \end{pmatrix}
\end{aligned}$$

The probabilities of finding the particle in well 1 and well 2 are given by the magnitude square of the corresponding coefficients of ψ_1 and ψ_2, respectively, and are thus given by

$$P_1 = \cos^2(\omega t) \qquad P_2 = \sin^2(\omega t) \qquad \omega = \epsilon/\hbar$$

Note that $P_1 + P_2 = 1$, as required by normalization, and that P_1 and P_2 vary sinusoidally from zero to one. In fact, P_1 drops from one down to zero at the same time that P_2 increases from zero up to one. After that, P_2 drops back to zero as P_1 increases back up to one. This repeats over and over again. Evidently, the particle is tunnelling back and forth

between the two wells. This, by the way, is reminiscent of a beat pattern when two wave sources emit at slightly different frequencies. In fact, the math is exactly the same.

- It is interesting that there are moments in time when the particle is known to be confined to well 2. The amount of time, τ, that it takes for the particle to completely tunnel over to well 2 for the first time (so that it has a probability of one of being found there) is given by $\omega\tau = \pi/2$, or

$$\tau = \frac{\pi/2}{\omega} = \frac{\pi/2}{\epsilon/\hbar} = \frac{(\pi/2)\hbar}{\epsilon} = \frac{h}{4\epsilon}$$

Recall that higher values of ϵ imply a lower barrier, which in turn, implies a shorter transition time between the wells. That is evident from our calculations.

- We close this section with a discussion of the *unequal* double well potential, where the corresponding single-well states ψ_1 and ψ_2 have different energies. This has applications in a discussion of covalent bonds between different elements, where the shared electron may be more bound to one atom than to the other. In an extreme case, the result would be an ionic bond, where a valence electron originally from one atom is not shared between the bonded atoms, but is instead stolen by the other atom because of its higher electron affinity.

- In this case, the Hamiltonian matrix can be written

$$\hat{H} = \begin{pmatrix} E_0 - \delta & \epsilon e^{i\phi} \\ \epsilon e^{-i\phi} & E_0 + \delta \end{pmatrix}$$

where $E_0 - \delta$ and $E_0 + \delta$ represent the single-well energies of ψ_1 and ψ_2, respectively. Note that ψ_1 has a lower energy than ψ_2; this is an arbitrary choice.

- The stationary states of this system can be found by solving the time-independent Schrodinger Equation, again as a 2×2 matrix eigenvector/eigenvalue problem:

$$\begin{pmatrix} E_0 - \delta - E & \epsilon e^{i\phi} \\ \epsilon e^{-i\phi} & E_0 + \delta - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

Setting the determinant of this matrix to zero yields the energy levels

$$E_{\text{low}} = E_0 - \sqrt{\epsilon^2 + \delta^2} \qquad E_{\text{high}} = E_0 + \sqrt{\epsilon^2 + \delta^2}$$

- Plugging these values of E back into the matrix equation above allows us to solve for the stationary states themselves. For the lower energy state, we get $\epsilon e^{-i\phi} c_1 = -\gamma c_2$, and for the higher energy state, we get $\epsilon e^{i\phi} c_2 = \gamma c_1$, where $\gamma = \delta + \sqrt{\epsilon^2 + \delta^2}$ (note: $-\delta + \sqrt{\epsilon^2 + \delta^2} = \epsilon^2/\gamma$). Imposing the normalization condition $|c_1|^2 + |c_2|^2 = 1$ yields the stationary states:

$$\psi_{\text{low}} = \frac{1}{\sqrt{\epsilon^2 + \gamma^2}} \begin{pmatrix} \gamma \\ -\epsilon e^{-i\phi} \end{pmatrix} \qquad \psi_{\text{high}} = \frac{1}{\sqrt{\epsilon^2 + \gamma^2}} \begin{pmatrix} \epsilon \\ \gamma e^{-i\phi} \end{pmatrix}$$

- Note that $\gamma > \epsilon$, and so the particle is more likely to be in well 1 in the lower energy state, and is more likely to be in well 2 in the higher energy state. This is to be expected, since in the absence of tunnelling, ψ_1 is the lower energy state.

- If $\delta \gg \epsilon$ (the energy separation between ψ_1 and ψ_2 is much greater than the tunnelling parameter ϵ), then ψ_{low} is nearly identical to ψ_1 and ψ_{high} is nearly identical to ψ_2. Evidently, tunnelling can be neglected in this case, and ψ_1 and ψ_2 are essentially the stationary states of the system with energies nearly equal to $E_0 - \delta$ and $E_0 + \delta$, respectively.

- On the other hand, if $\epsilon \gg \delta$ (tunnelling effects are significantly greater than the energy difference between ψ_1 and ψ_2), then γ is very nearly equal to ϵ, and the stationary states and energy levels resemble what we got for the equal double well potential.